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# Provenance, depositional setting, and crustal evolution of the Cathaysia Block, South China: Insights from detrital zircon U-Pb geochronology and geochemistry of clastic rocks

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## Abstract:

We report the results of a combined study of detrital zircon U-Pb geochronology and bulk-rock elemental geochemistry on late Neoproterozoic to Cambrian clastic sedimentary rocks from South Jiangxi within Cathaysia. These clastic rocks are characterized by moderate chemical index of alteration (CIA) values of  $73 \pm 5.9$  and high Th/U ratios ( $>3.8$ ), indicating moderate weathering of the source area. The relatively high index of compositional variability (ICV = 0.62–1.30) values indicate a source compositionally dominated by immature material that lacks alumina-rich minerals. Bulk-rock major and trace element systematics on discrimination diagrams are consistent with the source provenance being felsic-intermediate igneous rocks of ancient continental crust origin. The geochemistry is also consistent with the clastic sedimentary rocks being deposited in a setting at or in the vicinity of passive continental margins. Detrital zircon U-Pb ages of the clastic rocks record five major age populations: 2614–2376 Ma (peak at  $\sim 2482$  Ma), 1953–1353 Ma, 1000–900 Ma (peak at  $\sim 958$  Ma), 850–730 Ma (peaks at  $\sim 845$  and  $763$  Ma) and 685–571 Ma (peak at  $\sim 635$  Ma). The age data provide a record of igneous activity in the source provenance: the 2482 Ma peak is consistent with the global Neoarchean continental crust growth; the 1953–1353 Ma population correlates with the period of assembly and breakup of the Columbia supercontinent; the prominent peak at  $\sim 958$  Ma corresponds to a common thermal-tectonic event associated with the assembly of Rodinia and the 850–730 Ma population is consistent with the breakup of the Rodinia supercontinent. The  $\sim 850$  Ma age is indicative of initial stage of Rodinia breakup in South China. Our data also reveal a 670–530 Ma population that correlates well with the Pan-African event associated with the formation of the Gondwana supercontinent, although no direct geological evidence for this event has been found within the SCB. Moreover, complex zircon morphology and comparisons of detrital zircon U-Pb age spectra in a global context suggest the late Neoproterozoic–Cambrian sedimentary rocks in the Cathaysia Block must have sourced from an exotic source with magmatic activities of late Archean, Grenvillian and Pan-African ages, which do not outcrop in the Cathaysia Block or adjacent regions and need to be further explored.

**Keywords:** Geochemistry; Zircon U-Pb geochronology; Provenance; Tectonic; Crustal evolution; Cathaysia Block; South China

**Xiong, Chen,** Chen, Honde, **Niu, Yaoling,** Chen, Anqing, Zhang, Chenggong, Li, Feng, Xu, Shenglin & Yang, Shuai (2018). Provenance, depositional setting, and crustal evolution of the Cathaysia Block, South China: Insights from detrital zircon U-Pb geochronology and geochemistry of clastic rocks. *Geological Journal* 53(5): 1–16. [DOI: 10.1002/gj.3253]

## 1. Introduction

Geochemistry of (meta)clastic sedimentary rocks have been widely used to study the source provenance of sediments, and thereby to understand the geological evolution of continents concerned (e.g., Nesbitt and Young, 1982; Taylor and McLennan, 1985; Bhatia and Crook, 1986; McLennan et al., 1989; Fedo et al., 2003). Zircon is the most effective accessory mineral in geochronology because of its particular resistance to alteration and metamorphism, and thus faithfully preserves the initial isotopic compositions of its source magma at the time of crystallization (Fedo et al., 2003; Griffin et al., 2004). Particularly, detrital zircon ages have been successfully used as a powerful proxy to understand crustal evolution and to establish the inter-continental correlations and paleogeographic reconstructions of land masses within supercontinental assemblies (e.g., Fitzsimons, I.C.W., 2000a,b; Wang et al., 2003, 2010; Gehrels et al., 2006a,b; Yu et al., 2008, 2010; Condie et al., 2009; Wu et al., 2010; Yao et al., 2012, 2014, 2015a,b; Cawood et al., 2013; Xu et al., 2013, 2014). Therefore, an integrated study of geochemistry and detrital zircon U-Pb geochronology of sedimentary rocks can give valuable information.

Grabau (1924) suggested that metamorphic rocks widely distributed in southeastern China are of Archaean to Proterozoic age and overlaid unconformably by late Paleozoic strata. He coined the term of “Cathaysia Oldland” for all these rocks. The South China Block was formed by the amalgamation of the Cathaysia Block with the Yangtze Block (Fig.1a) in the Neoproterozoic, leading to the Jiangnan orogeny (Wang et al., 2003; Shu et al., 2011; Zhao and Cawood, 2012). The Jiang-Shao Fault (JSF) is considered to be the major suture zone between the two blocks, in which large amount of Meso-Neoproterozoic arc related volcanic and sedimentary rocks have been documented (Shu et al., 2006; Wong et al., 2011; Yao et al., 2015b). In recent years, significant research on zircon geochronology and geochemistry from the Precambrian to Paleozoic sedimentary rocks in the Cathaysia and Yangtze Blocks has offered insights into their Precambrian crustal evolution, tectonic affinity with other blocks, as well as the refinement of previous tectonic models for the South China Block (e.g., Sun et al., 2009; Li et al., 2010; Wang et al., 2010; Xiang et al., 2010; Yu et al., 2010; Yao et al., 2012, 2014; Zhao and Cawood, 2012; Shu et al., 2014). The geodynamic evolution of the South China Block has been recognized to have a close link to Columbia, Rodinia and Gondwana supercontinent cycles (Zhao et al., 2002; Zhou et al., 2002a, b; Yu et al., 2008; Shu et al., 2011; Yao et al., 2012, 2015a,b; Cawood et al., 2013; Li et al., 2014). However, important questions remain to be addressed: (1) does the Cathaysia Block have a Neoproterozoic crystalline basement? (2) what was the relationship between the Cathaysia and Yangtze blocks in the late Neoproterozoic? (3) what are the manifestations of the supercontinents (such as the Columbia, Rodinia) in South China Block? (4) does the South China Block have any record of the Pan-African orogenesis?

In order to address some of these questions, we take a geochemical (bulk-rock compositions) and geochronological (detrital zircon age dating) approach on clastic sedimentary rocks from the Chongyi area southeast of the Jiangshan-Shaoxing fault and

northwest of the Zhenghe-Dapu fault in the Cathaysia Block (Fig. 1), where the Neoproterozoic and Cambrian strata are well exposed for such a study. In this paper, we present the results of this study, which place constraints on the provenance and depositional setting of the sediments in the Cathaysia Block and shed light on its crustal evolution and tectonic affinity to other tectonic blocks.

## 2. Geological background

The South China Block (SCB), one of the largest Precambrian tectonic blocks in eastern Asia, comprises the Yangtze Block in the northwest and the Cathaysia Block in the southeast. The two continental blocks are separated by the NE trending Jiangshan-Shaoxing Fault (JSF) at the eastern end while its western extension is unclear due to the poor exposure and tectonic modification (Fig.1a, Yao et al., 2015b). The Cathaysia and Yangtze Blocks have different crystalline basements and tectonic histories (Yao et al., 2011; Zhao and Cawood, 2012). The Yangtze Block comprises a spatially limited Archean-Paleoproterozoic crystalline basement, surrounded by Mesoproterozoic to early Neoproterozoic fold belts. The latter is regionally overlain unconformably by low grade Neoproterozoic strata and an unmetamorphosed Sinian cover succession (Zhao and Cawood, 2012). The Kongling Complex, the oldest metamorphic basement in the Yangtze Block, is dominated by Archean TTG gneisses with formation ages of ca. 3.4-3.2 and 3.0-2.9 Ga (Gao et al., 2011). The Cathaysia Block is dominated by Phanerozoic igneous rocks (especially Mesozoic granitoids) and sedimentary rocks with Precambrian basement sparsely exposed in the Wuyishan, Nanling and Yunkai along a NE-SW belt bounded by the Jiangshan-Shaoxing Fault to the northwest and the Zhenghe-Dapu Fault in the southeast. Few Precambrian metamorphic rocks crop out in the coastal region, east of the Zhenghe-Dapu Fault, because of the extensive and intensive Mesozoic volcanic and granitoid rocks. Besides, whether or not there exists Archean basement in the Cathaysia Block is still under debate. Some believe the presence of Archean basement because of inherited/captured zircons in the Mesozoic magmatic rocks as well as detrital zircons in the Cathaysia Block (e.g., Yu et al., 2008, 2010; Wu et al., 2010; Zhao and Cawood, 2012), whereas others suggest that detrital zircons are widespread and possibly came from an exotic Archean source provenance once adjacent to the Cathaysia Block (e.g., Li et al., 2014).

The collision between the Yangtze and Cathaysia Blocks completed the formation of the South China Block in the early Neoproterozoic as expressed by the Jiangnan orogen in the SE-margin of the Yangtze Block (Li et al., 2002). The post-collisional process of the Jiangnan orogeny is characterized by some 850-800 Ma mafic-ultramafic bodies (SHRIMP zircon U-Pb) (Li et al., 2005; Shu et al., 2011) and numerous peraluminous granitic plutons with U-Pb ages of 830-790Ma (Wang et al., 2006, 2013; Li et al., 2009). Subsequently, a regional scale rifting occurred both in the Jiangnan belt and in the Cathaysia Block. This rifting was related to the breakup of the entire South China Block and the Cathaysia Block was broken up into three sub-blocks, namely, Wuyi, Nanling and Yunkai domains, as a response to the breakup of Rodinia supercontinent, and triggered the eruption of bimodal volcanic rocks of 810 - 790 Ma (e.g., Wang et al., 2003; Li et al., 2005; Yu et al., 2010). The areas between these sub-blocks evolved from a continental rift into shallow basins infilled with Cryogenian-Ordovician clastic sedimentary rocks, which is interpreted to mark the breakup of the South China Block (Li et al., 2005; Xiang et al., 2010; Yao et al., 2012). In the Wuyi domain, Mesoproterozoic migmatitic gneisses, granitic gneisses, schists, granulite, and leucopleite are exposed, together with Neoproterozoic clastic rocks, spilite, basalt, and rhyolite, among other units. Within the Nanling and Yunkai domains, Proterozoic clastic rocks,

which are variably metamorphosed, are widely exposed (Shu, 2006).

In the middle Neoproterozoic, the rifting stopped and the entire South China Block subsequently entered into a stable depositional environment. However, the sedimentation patterns of the Yangtze and Cathaysia Blocks during the late Neoproterozoic and early Paleozoic are different (Liu and Xu, 1994; Yao et al., 2014). From the Sinian (latest Neoproterozoic) to early Paleozoic, much of the Yangtze Block is dominated by carbonate and argillaceous carbonate/dolomite. In the eastern Yangtze Block, between the JSF and Anhua-Luocheng faults, Neoproterozoic units include clastic rocks intercalated with bimodal volcanic rocks, tillites, siliciclastic rocks and carbonate rocks (limestone and dolomite). The Cambrian strata are consisted of shale-silicalite and carbonate rocks, indicating a shallow sea setting without major elevated land areas to provide significant terrestrial detritus during the late Neoproterozoic to early Paleozoic. In contrast, the Cathaysia Block is dominated by shallow-marine siliciclastic rocks. The Neoproterozoic stratigraphic sequence domain is an association of meta-sandstone, siltstone and mudstone intercalated with lenticular limestone and the Cambrian strata are dominated by feldspathic sandstone and mudstone (Fig. 1b; Liu et al., 1994; Chen et al., 2006; Wang et al., 2010; Yao et al., 2014).

### 3. Sampling and analytical methods

This study focuses on the late Neoproterozoic to Cambrian strata from which we selected 36 fresh clastic sedimentary rocks on well-known outcrops in the Chongyi area, 24 of Cambrian age (D38-1-D47-3) and 12 of Sinian age (D48-1-D50-3). About 5 kg of representative material from two samples were selected (D38-5 and D50-2) for zircon separation. All the samples have similar mineralogy of quartz and plagioclase with minor mica, matrix and silicate cements (see sample details in Supplementary Table 1).

For geochemical analysis, veins, alteration and weathering products were avoided during sample preparation. Samples were cleaned and crushed into 200 mesh powder in tungsten carbide steel mill. All the powdered samples were baked at 105°C for twelve hours. Major and trace elements were measured at the Key Laboratory of Nuclear Techniques in Geosciences of Sichuan Province, China. The sample powders were mixed with seven times the amount of  $\text{Li}_2\text{B}_4\text{O}_7$  to make glass discs to be analyzed for major elements using X-ray fluorescence (XRF). On the basis of USGS rock standard (BIR-1, BCR-2, BHVO-2) analyses, the analytical precision and accuracy were better than 5%. Trace elements were analyzed using the Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) following Liu et al. (1996). The precision of the ICP-MS analysis is better than 10% for all trace elements.

Sample D38-5 and D50-2 was crushed to a 60 mesh powder and zircon grains were separated by using heavy-liquid and magnetic methods and purified by handpicking under a binocular. Representative zircon grains were handpicked and mounted in epoxy resin discs before polished and coated with gold. Cathodoluminescence (CL) images of the zircons were used to reveal zircon internal zoning and to select optimal spots for U-Pb dating. U-Pb zircon dating was conducted by using LA-ICP-MS at the Wuhan SampleSolution Analytical Technology Co., Ltd., China following Zong et al. (2017). Laser sampling was performed using a GeolasPro laser ablation system that consists of a COMPexPro 102 ArF excimer laser (wavelength of 193 nm and maximum energy of 200 mJ) and a MicroLas optical system. An Agilent 7700e ICP-MS instrument was used to acquire ion-signal intensities. Helium was applied as a carrier gas. Argon was used as the make-up gas and mixed with the carrier gas via a T-connector before entering the ICP. A “wire” signal smoothing device is included in this laser ablation system (Hu et al., 2015). The spot size and frequency of the laser were set to 32  $\mu\text{m}$  and 5Hz, respectively. Zircon 91500 and glass NIST610 were used as external standards for U-Pb dating and trace element calibration, respectively. Each analysis was done

with background acquisition of ~20-30s followed by 50s of data acquisition. An Excel-based software ICPMSDataCal was used to perform off-line data reduction (Liu et al., 2008). Concordia diagrams and weighted mean ages were done using Isoplot/Ex\_ver3 (Ludwig, 2003).

## 4. Analytical results

### 4.1. Whole rock geochemistry

The bulk-rock major and trace element analyses are given in Supplementary Table 1. Major element data are characterized by intermediate to high  $\text{SiO}_2$  (60.58 - 83.01 wt%), intermediate  $\text{Al}_2\text{O}_3/\text{SiO}_2$  (0.10-0.32) and  $\text{MgO}+\text{Fe}_2\text{O}_3$  contents (3.49-11). In addition, all the samples have relatively low CaO (0.01-1.17 wt% and mostly lower than 0.5 wt%) and high  $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O}+\text{CaO})$  (typically >5), which is consistent with the petrography without carbonate minerals.

Trace elements are also highly variable in concentration (Supplementary Tables 2 and 3). The chondrite-normalized REE patterns generally display a pronounced LREE enrichment and flat in HREE (Fig. 2a) with varying  $\text{La}_\text{N}/\text{Sm}_\text{N}$  (3.37-5.00),  $\text{Gd}_\text{N}/\text{Yb}_\text{N}$  (1.25-2.71) and  $\text{La}_\text{N}/\text{Yb}_\text{N}$  (6.63-19.60) ratios. Although the absolute concentrations of REEs are variable between samples, all samples show the same chondrite-normalized patterns resembling that of the average PAAS (Fig.2a; McLennan, 1989) with a distinctive negative Eu anomaly ( $\text{Eu}/\text{Eu}^*=0.46\text{-}0.66$ ). On upper continental crust (Taylor and McLennan, 1985) normalized multielement diagram, all the samples exhibit uniform patterns with a pronounced Sr depletion (Fig.2b). Compared to the PAAS, most of our samples are relatively enriched in large ion lithophile elements (LILE) such as Th and U, and relatively lower in Rb. The samples are relatively enriched in some high field strength elements (HFSE) such as Zr and Hf, but variably depleted in others like Nb and Ta.

### 4.2. CL images and Th/U ratios

Zircons of this study are characterized by light brown to colorless, and transparent to semitransparent. Cathodoluminescence (CL) images clearly show that most of the analyzed zircons have varying size (76 to 225  $\mu\text{m}$ ) with strong oscillatory zoning, sector/planar zoning or no zoning. Representative CL images of the detrital zircons together with spot ages are shown in Figure 3. Some of the zircons show moderately to highly rounded grain morphology with abrasive imprints, indicative of long-distance transport or multiple cycling (Fig. 3). Other grains are euhedral to subhedral, implying limited transport from their source region.

The Th/U ratio of zircons has been commonly used to distinguish zircons of magmatic and metamorphic origins (e.g., Maas et al., 1992). Zircons with high Th/U ratios (often larger than 0.4) are generally considered to be magmatic, whereas those with low Th/U ratios (<0.1) are thought to have grown under metamorphic conditions (Corfu et al., 2003; Hoskin and Black, 2003). However, it is not straightforward to distinguish between zircons of igneous and metamorphic origin based exclusively on the Th/U ratios because there are exceptions; some

igneous zircons show low Th/U and vice versa. Nevertheless, the Th/U ratios offer a broad estimate on the origins of zircons. The majority of zircons in this study show oscillatory zoning, and 107 grains among the 152 zircon U-Pb ages have Th/U > 0.4 with only 6 grains having Th/U < 0.1, indicating that zircons in our samples are mostly derived from magmatic rocks. Thus, the ages of the igneous zircons represent the timing of their crystallization. A few grains display bright structureless characters with Th/U < 0.1 interpreted to be of metamorphic origin.

#### 4.3. U-Pb ages of detrital zircons

One hundred and fifty-two zircons from two samples D38-5 and D50-2 were dated. The LA-ICP-MS age data are given in Supplementary Table 4 and all of the analyses are plotted on the Concordia diagrams (Fig. 4). Most of the U-Pb ages are concordant. Uncertainties on individual analyses in the data table and concordia plots are presented at  $1\sigma$ , and those analyses with more than 10% discordance were not included in frequency diagrams (Fig. 4c). Because  $^{207}\text{Pb}/^{206}\text{Pb}$  ages are commonly considered to be more reliable than  $^{206}\text{Pb}/^{238}\text{U}$  ages for zircons older than 1000 Ma (Compston et al., 1992), we used the  $^{207}\text{Pb}/^{206}\text{Pb}$  ages for such older zircons (> 1000 Ma), and  $^{206}\text{Pb}/^{238}\text{U}$  ages for younger zircons (<1000 Ma) in the following discussion.

The detrital zircon grains from the two sandstone samples yielded concordia ages in the range of 635–3176 Ma (Supplementary Table 4). This wide range of ages emphasizes the great diversity of rocks in the source areas. Broadly, the U-Pb ages are concentrated in four groups: 2614–2376, 1953–1353, 1000–900, 850–730 and 685–571 Ma. On age spectra, the most prominent age peak appears at ca. 958 Ma, followed by the peaks at ca. 635 Ma, 763 and 845 Ma. The age peak at about 2482 Ma is also relatively prominent. Our samples also show Archean zircons as represented by 11 U-Pb ages older than 2.5 Ga, with the oldest  $^{207}\text{Pb}/^{206}\text{Pb}$  concordia age at  $3176 \pm 28$  Ma. According to the youngest concordant age, which implying an upper limit age for the deposition of sedimentary rocks (Sun et al., 2008), the depositional time of the two samples were later than  $584 \pm 5$  Ma.

### 5. Discussion

#### 5.1. Nature of source rocks

Although the chemical composition of clastic sedimentary rocks can be influenced by many factors such as source rock, chemical weathering, sorting during transport and sedimentation, diagenesis and regional metamorphism, geochemical characteristics of sedimentary rocks can be powerful tools to elucidate source rocks (e.g. Nesbitt and Young, 1982; Taylor and McLennan, 1985; McLennan et al., 1989, 1995). The chemical index of alteration (CIA) and the index of compositional variability (ICV) provide useful measures to trace the source rocks and provenance of sediments (e.g., Nesbitt and Young, 1982; Cullers and Podkovyrov, 2000; Gu et al., 2007). The CIA values for our samples range from 64 to 87 (average of 73),

suggesting a moderate weathering history for the source rocks. It is similar to those of the post-Archean shales and the North America shale composite (CIA = 70-75; Taylor and McLennan, 1985), suggesting that the effects of weathering had not proceeded to the stage where alkali and alkaline earth elements are substantially removed from the clay minerals. Th/U ratios ( $> 4$ ) are related to the weathering history (McLennan et al., 1995). Samples from this study have variable but generally high Th/U ratios, typically above the upper crustal value of 3.8, also suggesting a moderate weathering. The relatively high ICV (0.62-1.30, average 0.93) in our samples indicates they were derived from a source compositionally immature and poor in alumina-rich minerals (Fedo et al., 1995).

The chemical compositions of sedimentary rocks are one of the most reliable indicators of source rocks (Taylor and McLennan, 1985; McLennan, 1989; McLennan et al., 1995). In weathered igneous rocks, Al tends to be enriched in mica and clays and residual feldspars, while Ti and Fe are mostly hosted in mafic minerals (Hayashi et al., 1997). Therefore, the ratio of Al/Ti can be a good indicator for protolith composition. Girty et al. (1996) proposed that  $\text{Al}_2\text{O}_3/\text{TiO}_2$  is useful to determine the provenances of clastic sedimentary rocks, which, with  $\text{Al}_2\text{O}_3/\text{TiO}_2 < 14$ , most likely reflect a mafic source, while sedimentary rocks with  $\text{Al}_2\text{O}_3/\text{TiO}_2 = 19$  to 28 suggest a felsic source. The  $\text{Al}_2\text{O}_3/\text{TiO}_2$  ratios for most of our samples range from 16 to 28 (average 19.11, supplementary Table 1), indicating the source area was dominated by felsic rocks.

Trace elements (e.g., REEs, Th, Zr, Hf) with relatively low mobility during sedimentary processes and low residence time in seawater are particularly sensitive to its sediment provenance, which can be used to indicate the nature of the source (e.g., Taylor and McLennan, 1985; Bhatia and Crook, 1986; McLennan et al., 1989). Generally, mafic rocks will show low REE differentiation with no Eu to positive Eu anomalies; whereas rocks derived from upper continental crust are always enriched in LREE with high  $\text{La}_N/\text{Yb}_N$  ratios (e.g., El-Bialy, 2013) and negative Eu anomalies. The significant enrichment of LREEs, distinctive negative Eu anomalies and flat HREE patterns of our samples (Fig.2a) suggest their derivation from an old upper continental crust composed chiefly of felsic lithologies. Of the elements considered, Th is more immobile than Sc. Sc/Th and La/Sc ratios are particularly sensitive to average source composition, and thus can be used to distinguish between mafic/ultramafic and felsic components (Taylor and McLennan 1985; Wronkiewicz and Condie 1987). Our study shows that all our samples have relatively high La/Sc (4.55) and low Sc/Th (0.59) ratios. This indicates a more likely derivation from a source dominated by felsic rocks, which is also consistent with the low Co and Cr contents (Table 1).

Other trace element characteristics of sedimentary rocks also place some constraints on the nature of the source. Floyd and Leveridge (1987) used a La/Th vs. Hf plot to discriminate between different source compositions. In Fig.5a, most samples lie within the felsic source, with increasing old sediment component. This indicates a derivation from felsic rocks with significant contribution of old continental crust material. The Co/Th vs. La/Sc plot (Fig.5b) also reflects a mixed source, dominated by felsic materials (e.g., McLennan and Taylor 1984; Taylor and McLennan 1985). Moreover, the plot of  $\text{TiO}_2$  vs. Ni (Fig. 5c) indicates that clastic



rocks are sourced from felsic magmatic rocks. Floyd and Leveridge (1987) and McCann (1991) used a  $K_2O$ -Rb plot to distinguish the nature of sources between felsic/intermediate and basic compositions. As shown in Figure 5d, the significant K-Rb correlation indicates our sample derivation from predominantly felsic/intermediate source rocks. In addition, in the ternary diagrams of Th-Hf-Co and La-Th-Sc (Fig.6), all the samples cluster between the average composition of felsic to intermediate components but far from the basalt end member. Thus, we infer that the source of the late Neoproterozoic-early Paleozoic sediments were dominantly derived from felsic-intermediate provenance characteristic of old continental crust material.

## 5.2. Implication for the depositional setting

Bulk-rock major and trace elements have proven to be a powerful tool in characterizing tectonic settings of sedimentary deposition (e.g., Bhatia, 1983; Bhatia and Crook, 1986; Roser and Korsch, 1986). The discriminant function plot of 11 major elements of Bhatia (1983) was used here (Fig. 7). In the Figure 7a, most samples fall in the field of passive continental margin. This agrees with the tectonic discrimination by using other methods (Figs. 7b,c; Roser and Korsch, 1986; Maynard et al. (1982). Bhatia and Crook (1986) use La-Th-Sc, Th-Co-Zr/10 and Th-Sc-Zr/10 diagrams (Fig. 8) to distinguish sandstones derived from different tectonic settings and provenance fields. Our samples are scattered in the fields of active continental margin, passive margin and continental arc. This result is somewhat different from discrimination using major elements (Fig. 7), which indicates a passive margin depositional setting. This discrepancy between discrimination diagrams may reflect a complex nature of tectonic settings and also short-comings of some discrimination diagrams. However, the chondrite-normalized REE pattern involving the most sensitive tectonic discriminant parameters also supported the passive margin depositional setting. It is evident by high enrichment of LREE over HREE with pronounced negative Eu anomaly, which is in contrast to different patterns in active continental margin/continental arc setting (Table 2 and Fig. 2a, Bhatia, 1986). We note that continental arcs (CA) and active continental margins (ACM) are the same setting manifested by the present-day Andes in South America. Also, CA/ACM and PM may not be effectively distinguished if basement rock supply is locally more significant than rocks of active volcanism at a CA/ACM environment (also see below).

This discrepancy of using trace elements in this study may reflect inherited signatures of the clastic sediments from old provenance terranes (e.g., ancient basement of active continental margins) rather than its depositional environment (e.g., Savoy et al. 2000; Bai et al., 2007; Concepcion et al. 2012). The U-Pb detrital zircon dating of the sandstone samples is dominated in Neoproterozoic to Mesoproterozoic, much older than their depositional age (Sinian-Cambrian) confirms this hypothesis. Hence, it may indicate that the tectonic settings derived from Figure 8 in this study represent the tectonic setting of the old provenance terrane, which is supported by previous work on the tectonic evolution of the SCB (e.g., Li et al., 2003; Shu et al., 2006, 2011; Yao, et al., 2011, 2014; Zhao et al., 2012). Therefore, on the

basis of bulk-rock geochemistry and detrital zircon age data, we conclude that a passive continental margin setting best explains the deposition of the sandstone samples. The lack of magmatism and metamorphism during this period in the South China Block also confirms this scenario (e.g., Shu et al., 2006; Yu et al., 2008; Zhao et al., 2012; Li et al., 2014).

### 5.3. Provenance and Crustal evolution of the Cathaysia Block

The age spectra of detrital zircons from the late Neoproterozoic-early Paleozoic sedimentary rocks of the western Cathaysia Block reveal five prominent Precambrian age populations: 2614-2376 Ma (peak at ca. 2482 Ma), 1953-1353 Ma, 1000-900 Ma (peak at ca. 958 Ma), 850-730 Ma (peaks at ca. 845 and 763 Ma) and 685-571 Ma (peak at ca. 635 Ma) (Fig.9), providing new data to study the provenance characteristics and crustal evolution of the Cathaysia Block.

The late Archean age populations (i.e., 2614-2376 Ma) coincide with the timing of global crustal growth at the end Archean-early Paleoproterozoic (e.g., Qiu and Gao, 2000; Zheng et al., 2006; Santosh et al., 2013). Detrital zircons with similar ages have been widespread in the Cathaysia Block (only one peak at ~2.44 Ga) and Yangtze Block (two peaks at 3.0-2.9 Ga and ~2.5 Ga) (e.g., Sun et al., 2009; Xiang et al., 2010; Wong et al., 2011). However, direct evidence of an Archean basement for the Cathaysia Block or the Yangtze Block has not been reported as yet. The Kongling Complex, the oldest Archean rocks exposed in the South China Block, has detrital zircon age spectra that is uniquely different and cannot be the provenance for the late Neoproterozoic-early Paleozoic sedimentary rocks we study (Fig.9; Gao et al., 2011, Guo et al., 2014). Most of the zircons with this ages are oval in shape with abrasive imprints (Fig.3), indicating long-distance transport from their source or complex multiple recycling histories. Thus, we infer that these Archean detrital zircons in the Cathaysia Block may come from exotic sources rather than the intra-basin erosion of basement rocks.

The relative probability plots of the U-Pb zircon ages display a small but broad age population of 1953-1353 Ma (Fig.4). This age peak broadly coincides with the assembly (during ca. 2.0-1.6 Ga) and breakup (during ca. 1.5-1.3 Ga) of Columbia supercontinent (e.g., Rogers and Santosh, 2002; Nance et al., 2014). Previous studies have identified amphibolite protolith of  $1766 \pm 19$  Ma within the Cathaysia Block (Li, 1997). Paleoproterozoic granitoids emplaced at 1860-1890 Ma have also been obtained in the Wuyi Mountains, northeastern Cathaysia (Yu et al., 2010; Yao et al., 2012). However, magmatic events of ca. 1700-1400 Ma are so far unknown within the South China Block. Granitoids and felsic volcanic rocks with an age of ~1450 Ma have only been identified from Precambrian rocks on Hainan Island (Li et al., 2008; Xu et al., 2014), but the latter, as part of the Chinese continental shelf, is of exotic origin (affiliated with western Australia) and joined the South China Block in the Cretaceous (Niu et al., 2015). Although the Paleo-Mesoproterozoic age population is no prominent, it has widely emerged in the age spectra of detrital zircons from the South China Block (e.g., Li, 1997; Yu et al., 2008; Xiang et al., 2010; Wang et al., 2010;

Wu et al., 2010; Shu et al., 2011; Yao et al., 2011; this study), suggesting that the South China Block was probably close to the Columbia supercontinent or even part of it during that time. In addition, complex morphological characteristics of these zircons indicate different provenances, some of which show moderately to highly rounded morphology with abrasive imprints, but others are euhedral to subhedral (Fig.3). Thus, we suggest that the detrital zircons were most likely derived from within the South China Block (e.g., northern Yangtze, Cathaysia Blocks) and input from multi-cycled sedimentary sources from neighboring regions once connected.

The 1000-900Ma age population stands out in the age spectra, which corresponds to the Grenvillian orogeny, related to the amalgamation of the Rodinia supercontinent (e.g., Cawood et al., 2013; Yao et al., 2014). There is a distinctive peak at ca. 958 Ma, suggesting that the studied zircons have captured information of a common important thermal-tectonic episode associated with the Grenvillian orogeny in South China. According to previous studies, the early Neoproterozoic magmatic activity was not significant for the Cathaysia Block and the exposure of Grenvillian rocks were limited in the whole South China, while zircons with similar ages are found to be widespread (e.g., Li et al., 2002; Yu et al., 2008; Wang et al., 2010; Wu et al., 2010; Wong et al., 2011). It is noteworthy that zircons of this age were mainly reported on metamorphic rocks. Li et al. (1995, 2002) have dated a Grenvillian metamorphic event (1.3-1.0 Ga) at the Sibao orogen between the Yangtze and Cathaysia Blocks. A metamorphic event at ca. ~1.0 Ga was also recorded in the trondhjemites and metapelites of the Kongling area, northwest South China and amphibole and biotite from the granulite in the Xichang area, west South China (Qiu and Gao, 2000; Xu et al., 2004; Zheng et al., 2006). Inherited zircons with ages ranging from 1070 Ma to 910 Ma have been recognized from the Guzhai granodiorite in Guangdong province (Wang et al., 2008). Tan et al. (2006) obtained a metamorphic record of 1035-900 Ma from the Yunkai Mountains of Guangdong Province. However, the 1.0-0.9 Ga zircons from the late Neoproterozoic-early Paleozoic sedimentary samples of this study show clear oscillatory zoning and moderately to highly rounded shapes (Fig.3), indicating a magmatic origin and long-distance transport with strong abrasion. Moreover, the reported 1.0-0.9 Ga igneous rocks in the western and northern margins of the Yangtze Block are dominated by mafic intrusions with rare felsic rocks, which rules out the possibility of a local source supply (Zhou et al., 2006; Sun et al., 2009). Through the reconstruction of Rodinia supercontinent in recent studies, the South China Block was suggested to have located close to Australia, and was believed to be part of east Gondwana during the Neoproterozoic and early Paleozoic (e.g., Zhou et al., 2002a; Yu et al., 2008; Wang et al., 2010; Duan et al., 2011; Shu et al., 2011; Cawood et al., 2013; Li et al., 2014; Yao et al., 2014). Together with the almost sea-water coverage of the entire SCB and the continuous northwest and west palaeocurrents during the late Neoproterozoic and early Paleozoic (e.g. Wang et al., 2010; Shu et al., 2012; Yao et al., 2014, 2015b), it is more likely that the large proportion of Grenvillian age zircon grains (1.0-0.9 Ga) with moderately to highly rounded shapes in our samples were derived from the once jointed blocks/terrane, rather than a local supply from within the South China Block.

Our age data from detrital zircons also show another cluster of middle Neoproterozoic ages (850-730 Ma), which is considered to be associated with the breakup of the Rodinia supercontinent (e.g. Zhao et al., 2002; Li et al., 2003; Shu et al., 2011; Zhai et al., 2011). Through comparing the intrusive dykes between South China and Australia, Li et al. (2003) concluded that the upwelling of mantle plume around 830 Ma resulted in the breakup of South China. However, recent studies established an age of ca. 849 Ma for the earliest anorogenic magmatism in the Yangtze Block (Li et al., 2009; Shu et al., 2011). The detrital zircon age spectra presented in our study show two clear peaks at 845 and 763 Ma, which probably are the manifestations of the initial stage of breakup of South China from the Rodinia and the dominant thermal event associated with the breakup of Rodinia, respectively. Postcollisional S-type granites, rift-related magmatic assemblages and collision-rifting tectonic process during the similar time were well recorded in the margins and interior of the Yangtze Block but quite limited in the Cathaysia Block (Wang et al., 2003; Xiang et al., 2010; Yu et al., 2010; Yao et al., 2011). Moreover, the episodes of middle Neoproterozoic thermal-tectonic event were also recorded in the Nanhua Basin (850-635Ma) with abundant zircons of 833-705 Ma ages (Fig.9; Wang et al., 2010; Yao et al., 2014, 2015b). The detrital zircons of this age in our study are markedly euhedral or subhedral, which suggests that they were mainly derived from local sources without long-distance transport, namely, from the margins and interiors of the Yangtze Block (such as the Jiangnan orogen).

The subordinate zircon peak at 635 Ma for the 685-571 Ma age population deserves special attention. The magmatic activity represented by this zircon age peak and range may be a response to the Pan-African event associated with the formation of the Gondwana supercontinent. The age peak at ca. 635 Ma in our data probably represents imprints of a distinct phase of thermal-tectonic event associated with the assembly of Gondwana. Although no direct evidence for a major Gondwana-related orogeny has yet to be found in the South China Block (e.g., magmatic, metamorphic or deformational records) during this period, the late Neoproterozoic ages obtained in this study suggest the existence of a provenance from which these detrital zircons were sourced. In fact, this age range correlates well with the ~ 650-500 Ma tectonism in east Gondwana, which may have provided coeval detritus zircons in the Himalaya regions (e.g., DeCelles et al., 2000; Gehrels et al., 2006a, b; Myrow et al., 2009; Duan et al., 2011). It is consistent with the northward paleocurrent in the central east Gondwana during the late Neoproterozoic to early Paleozoic (Myrow et al., 2010), which lead to the widespread detritus associated with the Pan-African event transport into the SCB. This is also supported by the similar Hf isotopic composition of detrital zircons from the SCB with the Paleozoic sediments in the India-Himalaya regions (e.g., Duan et al., 2011; Li et al., 2014). Hitherto, various configurations have been proposed for the timing and tectonic assembly of the Gondwana supercontinent (e.g., Wang et al., 2010; Duan et al., 2011; Cawood et al., 2013; Xu et al., 2013; Li et al., 2014; Yao et al., 2014). Some workers believed that the SCB is an isolated continent during the Neoproterozoic, far away from the northeastern margin of East Gondwana (e.g., Li et al., 1996; Zhou et al. 2002b). However, others suggested that South China is closely related to the Gondwana-forming orogeny (e.g., Duan et al., 2011; Cawood et

al., 2013; Xu et al., 2013; Yao et al., 2015b). The early Paleozoic shallow marine faunal affinities suggested that the SCB might have had its origin adjacent to the Himalaya region of the Gondwana margin (Rong et al., 2007; Peng et al., 2009). The latest Neoproterozoic rocks in the Lesser Himalaya and the SCB reveals remarkably similar tectonostratigraphic records (Jiang et al., 2003). Zhang et al. (2004) also provide paleomagnetic data indicating a long-term connection between the South China Block and Northern India during the assembly of Gondwana. These reports, together with the late Neoproterozoic and Cambrian aged detrital zircons with rounded-subrounded morphology in our samples, suggest that the South China Block should be linked with the northern India margin as a part of the Gondwana assembly, which served an exotic source for these early Paleozoic zircons.

#### 5.4. Tectonic affinity of the Cathaysia Block with other blocks

Detrital zircon geochronology has been widely used in tracing the provenances and their tectonic attributes (e.g., Cawood et al., 2000; Fedo et al., 2003; Griffin et al., 2004; Condie et al., 2009). For a better understanding of the tectonic history of the Cathaysia Block and its affinity with other major blocks, here we attempt a comparison of the age spectra between the Cathaysia Block and several ancient blocks (Yangtze, India-Himalaya region, west Laurentia, east Antarctica, southeastern Australia and western Australia, Fig. 9).

The relationship between the Yangtze and Cathaysia Blocks during the late Neoproterozoic and early Paleozoic has been a longstanding debate. Some proposed that the two Blocks share a unified continental terrane during that time (e.g., Wang et al., 2010; Cawood et al., 2013; Xu et al., 2013, 2014; Yao et al., 2015a), but others suggest the presence of an open ocean basin between the two until their reunion in the mid-Paleozoic (e.g., Shui, 1987; Liu et al., 1994; Xu et al., 1996; Wang et al., 2006). Comparison of detrital zircon age spectra for the late Neoproterozoic-early Paleozoic sedimentary samples from the eastern Yangtze and Cathaysia Blocks indicates their derivation from a similar provenance (Fig.9). Meanwhile, the correlated biostratigraphic and paleoecological evolution, facies analysis and paleocurrent measurements in the two blocks further indicate that they share a common continent without an open ocean in the late Neoproterozoic and early Paleozoic (e.g., Chen et al., 2006; Rong et al., 2007; Wang et al., 2010; Shu et al., 2014).

The continental nuclei growth during the Neoarchean-early Paleoproterozoic has been recorded worldwide (Zheng et al., 2006; Santosh et al., 2013). The 2.6-2.4 Ga zircons in our samples compare well with the detrital zircon age peaks of ~2.5 Ga for the Yangtze Block, India-Himalaya region, east Antarctica and southeastern Australia (Fig.9), suggesting a close tectonic affinity among these ancient blocks mentioned above, which is different from the dominant continental growth occurred at 2.8-2.6 Ga in west Laurentia and western Australia. An age range of ca. 1.95-1.35 Ga has been shown in our study, similar to the clear imprints of Paleo-Mesoproterozoic magmatism associated with the Columbia supercontinent in the Himalaya regions of India, west Laurentia and Australia. This suggests a possible tectonic affinity among them. However, the zircon ages in our samples are scattered along the age

spectra, indicating a relatively limited relationship between the Cathaysia Block and Columbia supercontinent. The Cathaysia Block, India-Himalaya region and east Antarctica all have detrital zircons of prominent 1.0-0.9 Ga with a strong peak at ca. 960 Ma, suggesting their close affinity with the assembly of Rodinia Supercontinent. Recent studies have recorded synchronous arcs in the Eastern Ghats belt of India and the Prince Charles Mountains of East Antarctica during the amalgamation of the Rodinia supercontinent (Fitzsimons, 2000a,b; Veevers, 2007). Whereas in other blocks like west Laurentia, southeastern Australia and western Australia, the Grenvillian event age of ~ 1300-1100 Ma is pronounced, indicating a diachronic nature of Rodinia assembly process (e.g., Li et al., 2002; Wang et al., 2008; Yao et al., 2011). Moreover, the Cathaysia, Yangtze, India-Himalaya region, Australia all show an obvious cluster peak at ~ 650-500 Ma, implying their close affinity with the Pan-African thermal-tectonic event associated with the assembly of Gondwana. This is consistent with the view that the South China Block must have connected with the margin of east Gondwana (e.g., Wang et al., 2010; Duan et al., 2011; Cawood et al., 2013; Xu et al., 2013; Yao et al., 2014), although no coeval magmatic rocks or related deformational events have been found as yet (e.g., Wang et al., 2008, 2010; Yu et al., 2010).

## 6. Conclusions

- (1) The late Neoproterozoic to Cambrian clastic sedimentary rocks from the Cathaysia Block in southeast China are characterized by moderate chemical index of alteration (CIA) values (average of 73) and the high Th/U ratios (>3.8), indicative moderate weathering of the source provenance. The relatively high index of compositional variability (ICV=0.62-1.30) values indicate a source compositionally dominated by immature material that lacks alumina-rich minerals. The bulk-rock major and trace element compositions indicate that the sedimentary sources are dominantly by felsic/intermediate magmatic rocks derived from ancient continent crust. The depositional environment is most probably at or in the vicinity of a passive continental margin.
- (2) Detrital zircons display five main age populations of 2614-2376 Ma (peak at ca. 2482 Ma), 1953-1353 Ma, 1000-900 Ma (peak at ca. 958 Ma), 850-730 Ma (peaks at ca. 845 and 763 Ma) and 685-571 Ma (peak at ca. 635 Ma), which correspond, respectively, to the Neoarchean global continental growth, the assembly and breakup of the Columbia supercontinent, the assembly of Rodinia, the breakup of South China from Rodinia and the Pan-African event associated with the formation of the Gondwana supercontinent. These finding-based interpretations form an important and testable hypothesis for future investigations.
- (3) Provenance analysis suggests the presence of abundant zircons of Neoarchean, Grenvillian and Pan-African ages in the Cathaysia Block, yet magmatic rocks of these ages are absent. These rocks may remain hidden in the basement or may have been largely recycled (without being preserved) in the geological history of the South China

Block. However, we consider it most likely that the sediments with the detrital zircons must have sourced from exotic continental terranes when they were once connected. This is supported by the zircon morphology of long distance transport.

- (4) This study offers important information towards better understanding the tectonic evolution of the South China Block in a global context (e.g., Columbia, Rodinia and Gondwana supercontinents) over Earth's Precambrian history.

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Fig.1. (a) Geological map of South China showing the distribution of Precambrian rocks in the Yangtze and Cathaysia Blocks and the sample location (after Zhao and Cawood, 2012) (b) Paleogeographic pattern and sedimentary facies of the South China Block during the early Paleozoic time (after Liu et al., 1994; Chen et al., 2006; Wang et al., 2010).

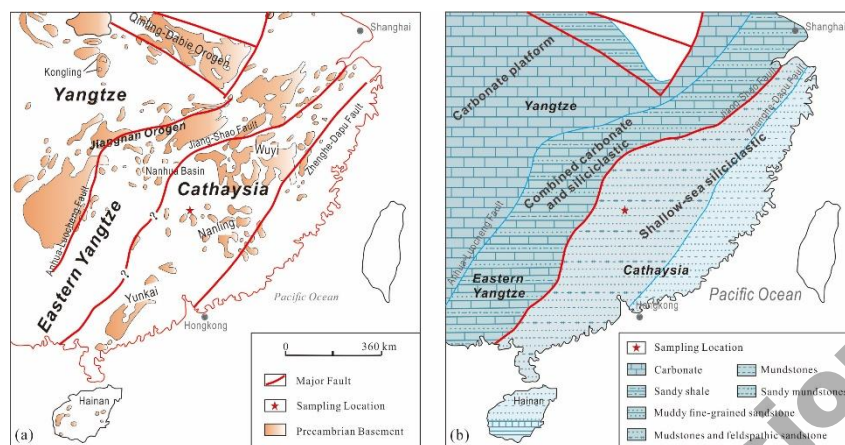


Fig.2. (a) Chondrite normalized rare earth element patterns for sedimentary rocks from the late Neoproterozoic to early Paleozoic in the Cathaysia Block. Normalized to chondritic values from Taylor and McLennan (1995). (b) Upper Continental Crust (UCC)-normalized multielement diagrams for samples from the late Neoproterozoic to early Paleozoic. UCC values are from Taylor and McLennan (1995). The standard composition of average Post-Archean Australian Shale (PAAS) after McLennan (1989) is shown for comparison; various tectonic conditions data after Bhatia (1986).

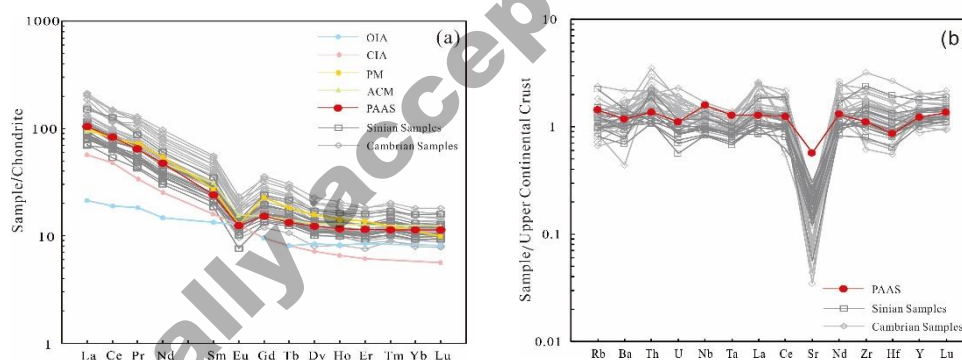


Fig.3. Representative cathodoluminescence images of selected detrital zircons with spots for analysis and ages given as indicated.



Fig.4. U-Pb concordia diagrams and probability density plot of LA-ICP-MS detrital zircon U-Pb ages from the late Neoproterozoic-early Paleozoic sandstone samples in the Cathaysia Block.

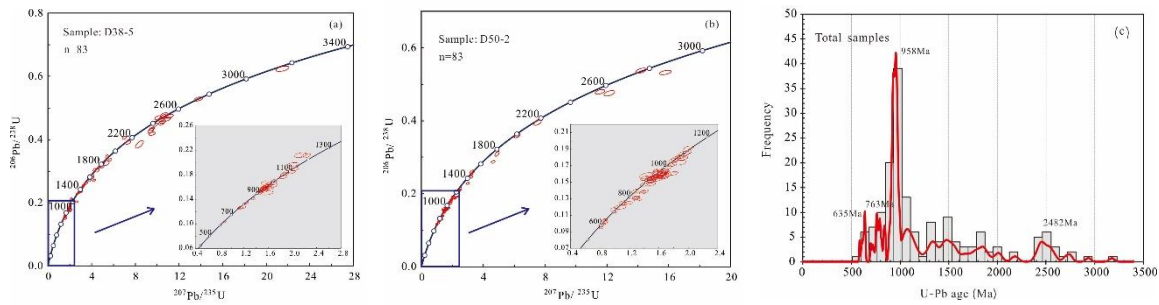


Fig.5 Source rock discrimination diagrams for sedimentary rocks from the late Neoproterozoic to early Paleozoic in the Cathaysia Block. (a) La/Th vs. Hf (after Floyd and Leveridge, 1987), (b) Co/Th vs. La/Sc (after Gu et al., 2002), (c)  $\text{TiO}_2$ -Ni (after Floyd et al., 1989) and (d)  $\text{K}_2\text{O}$ -Rb (after Floyd and Leveridge, 1987). Average reference compositions are from Condie (1993).

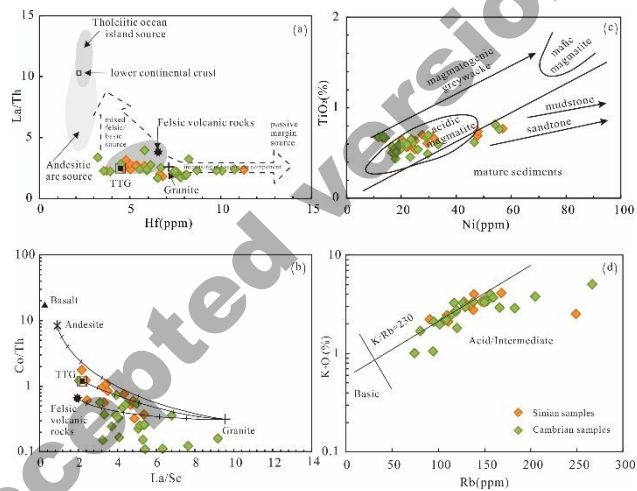


Fig.6. Plot of samples in Th-Hf-Co (left) and La-Th-Sc (right) ternary diagrams. Note that all the samples locate between the field of average Proterozoic granite and TTG, indicating mixture of these end members in the source. Average reference compositions are from Condie (1993).

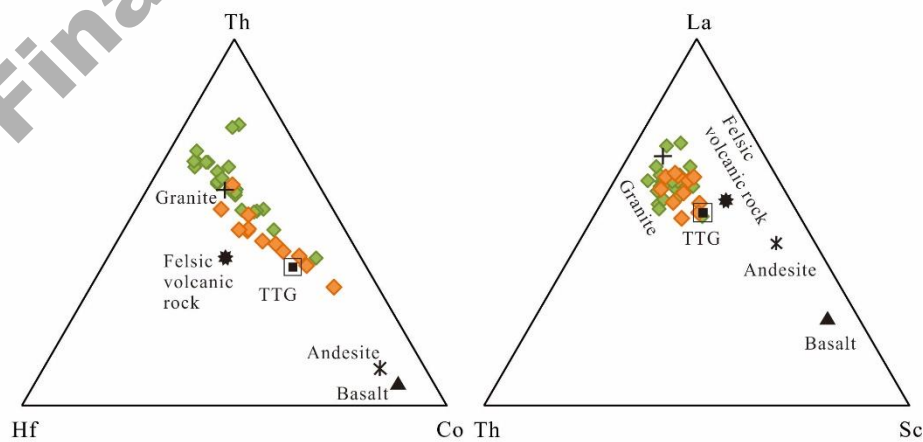




Fig.7. Tectonic setting discrimination diagram for sedimentary rocks. (a) Discriminant function plot (Bhatia, 1983), (b)  $\text{SiO}_2$  vs.  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  discrimination plot and (c)  $\text{SiO}_2/\text{Al}_2\text{O}_3$  vs.  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  discrimination plot (Roser and Korsch, 1986). OIC = oceanic island arc; CA = continental arc; ACM = active continental margin; PM = passive margin; A1 = island arc of basaltic and andesitic detritus; A2 = evolved island arc of felsic intrusive rock detritus. Symbols are as in Fig. 5.

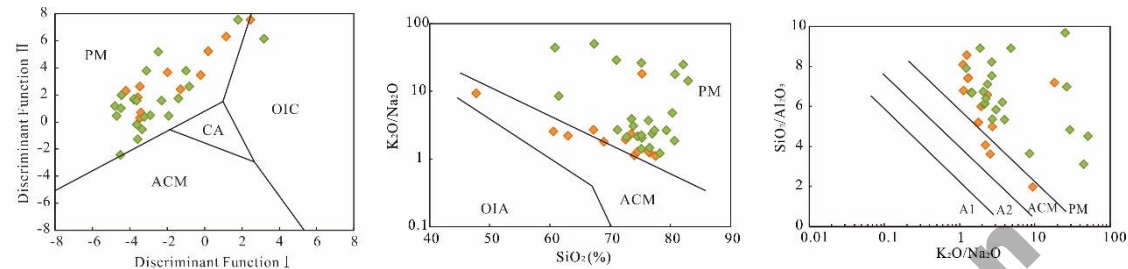


Fig.8. Tectonic discrimination ternary diagrams (Bhatia and Crook, 1986) used for the late Neoproterozoic-early Paleozoic sandstone samples in the Cathaysia Block: La-Th-Sc (left), Th-Co-Zr/10 (middle) and Th-Sc-Zr/10 (right). Symbols are as in Fig. 5.

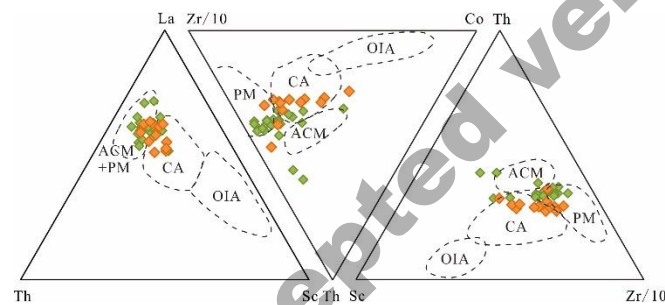


Fig.9. Relative probability diagrams of U-Pb detrital zircon age distributions for comparing from age-equivalent sedimentary samples of South China and outboard blocks, including Cathaysia, Yangtze, India-Himalaya region, West Laurentia, East Antarctica, Southeastern Australia and Western Australia. This study, Yu et al. (2008), Wu et al. (2010) and Yao et al. (2011) for upper Neoproterozoic-Ordovician strata in the Cathaysia Block; Wang et al. (2010) for Cambrian-Silurian sediments in the Easter Yangtze Block and Gao et al. (2011), Guo et al. (2014) for the Kongling complex; McQuarrie et al. (2008); Myrow et al. (2009, 2010); Zhu et al. (2011) for Paleozoic sediments in the Tethyan & Lesser Himalaya; Gehrels et al. (2006a, b) for the late Neoproterozoic in Great Himalaya; Dehler et al. (2010) for mid-Neoproterozoic sediments in West Laurentia; Boger et al. (2000), Carson et al. (2002), Kelly et al. (2002), Hokada et al. (2003) and Hokada et al. (2004) for Precambrian sediments in East Antarctica, Ireland et al. (1998) and Berry et al. (2001) for Neoproterozoic-Cambrian sediments in southeastern Australia and Cawood and Nemchin, (2000), Veevers et al. (2005) for Paleozoic sediments in Western Australia.

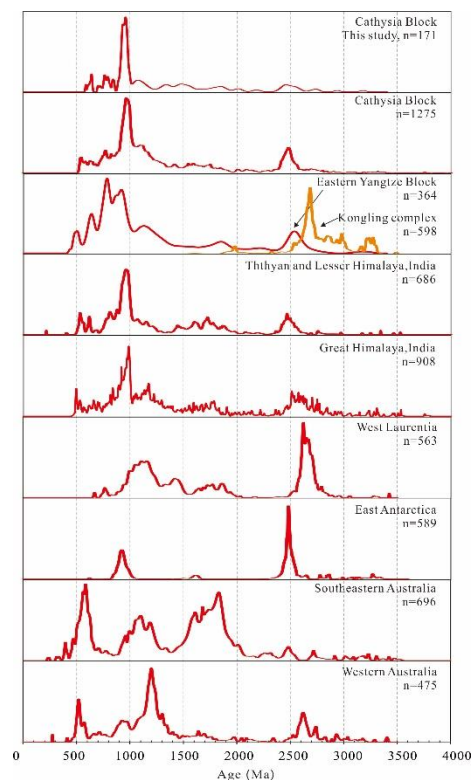




Table 1 Discriminating ratios of trace element for the sedimentary rocks from the late Neoproterozoic to early Paleozoic in the Cathaysia Block. Data from reference: Range of sediments from felsic sources and mafic sources (Cullers, 1994); UCC, Upper continental crust (Taylor and McLennan, 1985); LCC, Lower continental crust (Taylor and McLennan, 1985)

Ratio	This study	Range of sediment from mafic sources	Range of sediment from felsic sources	UCC	LCC
La/Sc	4.48	0.4–1.1	2.5–16	2.7	0.3
Sc/Th	0.60	20–25	0.05–1.2	1	34
Cr/Th	3.92	22–100	0.5–7.7	3.3	222
Co/Th	0.48	7.1–8.3	0.22–1.5	0.9	33

Table 2 Discriminating REE elements and ratios for the late Neoproterozoic-early Paleozoic sandstone samples in Cathaysia Block (after Bhatia, 1983).

Tectonic settings	La	Ce	REE	La/Yb	(La/Yb) <sub>N</sub>	$\sum_{\text{LREE}}/\sum_{\text{HREE}}$	Eu/Eu*
Oceanic island arc	8±1.7	19±3.7	58±10	4.2±1.3	2.8±0.9	3.8±0.9	1.04±0.11
Andean type continental margin	37	78	186	12.5	8.5	9.1	0.6
Continental arc	27±4.5	59±8.2	146±20	11±3.6	7.5±2.5	7.7±1.7	0.79±0.13
Passive margin	39	85	210	15.9	10.8	8.5	0.56
This study	45.51	86.98	209.20	15.72	10.62	9.27	0.57